

**Synthesis and Crystal and Molecular Structure
of *trans*-[PtCl₂(8-dqmp)₂]*
(8-dqmp = diethyl 8-quinolylmethylphosphonate)**

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Received September 30, 1998; revised March 23, 1999; accepted March 24, 1999

The complex *trans*-[PtCl₂(8-dqmp)₂] – *trans*-dichloro-bis(diethyl 8-quinolylmethylphosphonate-κN)platinum(II) – has been synthesized and the molecular structure has been determined by a crystallographic study. The platinum atom has a slightly distorted *trans* square-planar configuration with Pt1–N1 = 2.042(4) and Pt1–Cl1 = 2.306(1) Å. The dihedral angle between the Pt coordination plane and the mean plane of the 8-quinolylmethyl moiety is 65.1(1)°. The complex reveals a very interesting feature: a very short methylene proton–platinum distance of 2.309(5) Å occupying approximately axial positions around the central metal atom for the hydrogen atom H10B. Refinement was performed by least-squares methods to a final *R* value of 3.02%.

Key words: X-ray structure, platinum(II) complex, diethyl 8-quinolylmethylphosphonate, Pt–H interaction.

INTRODUCTION

There is a great interest in platinum(II) complexes not only because of their importance in organic synthesis and catalytic processes but also from

* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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the biological and pharmacological points of view. Rosenberg's discovery of the cell-division inhibiting activity exerted by cisplatin (*cis*-diaminedichloroplatinum(II)) toward *E. coli* bacteria initiated numerous fundamental studies of the coordination chemistry of platinum and palladium compounds. These complexes bind selectively to the nucleic acid bases in a monodentate or bidentate fashion, and they may form intra- and inter-strands crosslinks that disrupt the normal function of DNA.^{1,2} Structure-activity relationships have been defined for chemotherapeutic agents based on cisplatin. They claim the necessity of the *cis*-[PtX₂(amine)₂] structure, where X should be an anion with intermediate binding strength (such as Cl⁻, SO₄²⁻ or similar). The amine ligand should possess at least one N-H moiety, which is thought to be necessary for H-bonding interactions toward DNA.³ The requirement of an N-H moiety for antitumor activity has become a subject of debate since an increasing number of platinum compounds have appeared in the literature that violate this rule. Examples of platinum complexes containing no N-H moiety but displaying significant antitumor activity are complexes with bipyridyl crown ethers,⁴ platinum organoamides containing pyridine ligands,⁵ and complexes containing bis(imidazole) ligands.⁶

The empirical structure-activity relationships delineated that *cis* geometry is necessary for antitumor activity. When the amine is changed to a planar ligand such as pyridine, the cytotoxicity of the *trans* complex is dramatically enhanced in comparison with that of its *cis* isomer.⁷

Since the biological and chemical activity is greatly influenced by the structure of the ligands and looking for the ligands important in medicinal and biological systems, we started to investigate the platinum metal complexes with organophosphorus compounds that can exhibit bactericidal and herbicidal activity. The coordination chemistry of this class of ligands has drawn relatively little attention.^{8,9} Our previous work on complexes containing 2- and 8-quinolylmethylphosphonate esters as ligands for palladium complexes have been found to be cytostatic *in vitro* against animal and human tumor cell lines.^{10,11}

In this paper, we report the synthesis and X-ray crystal structure of *trans*-dichloro-bis(diethyl 8-quinolylmethylphosphonate-κN)platinum(II).

EXPERIMENTAL

The melting point was determined on a hot stage microscope and is uncorrected. The infrared spectrum was recorded on a Perkin Elmer 580 B spectrophotometer using KBr (4000–250 cm⁻¹) and Nujol pellets (400–200 cm⁻¹). Elemental analyses were performed by standard analytical methods in the Department of Physical Chemistry, Ruđer Bošković Institute. The magnetic susceptibility in the solid state was measured at room temperature by the standard Gouy method using a Cahn-Ventron RM-2 balance and CuSO₄·5H₂O as the susceptibility standard.

Preparation of Complex

Diethyl 8-quinolylmethylphosphonate (8-dqmp) prepared as previously described by condensation of diethyl sodium phosphite with 8-bromomethylquinoline,¹² was purified by distillation under reduced pressure prior to use. The *trans*-dichloro-bis(diethyl 8-quinolylmethylphosphonate-κN)platinum(II) complex was obtained by reaction of 8-dqmp with K₂[PtCl₄] (Aldrich) in aqueous-ethanol solution. To a stirred solution of 8-dqmp (0.189 g, 0.68 mmol) in ethanol (2 ml), a concentrated aqueous solution of K₂[PtCl₄] (0.140 g, 0.34 mmol) was added dropwise. The precipitate formed after a few days was separated, washed with acetone and dried in vacuo over P₂O₅. Yield: 0.120 g (45%).

Anal. Calcd. for C₂₈H₃₆N₂P₂O₆PtCl₂ (*M_r* = 824.53): C 40.78, H 4.40, N 3.40%; found: C 41.08, H 4.65, N 3.16%. Selected IR data ν_{\max} / cm⁻¹: 1600 w, 1517 m ($\nu_{\text{C=C}}$, $\nu_{\text{C=N}}$); 1258 s, 1242 m-s ($\nu_{\text{P=O}}$); 1061 s, 1028 vs ($\delta_{\text{P-O-C}}$); 345 w ($\nu_{\text{Pt-Cl}}$).

Crystals suitable for structure analysis were obtained by recrystallization from dry methanol and addition of dichloromethane.

X-ray Data Collection and Refinement

A yellow-green crystal of approximate dimensions 0.3 × 0.4 × 0.8 mm was used for data collection. Crystal data and refinement details of the structure are reported in Table I. Unit cell parameters and intensity data were obtained on a Siemens AED diffractometer using Ni-filtered Cu-K α radiation. Cell dimensions were determined by least-squares fitting of 30 centered reflections with θ ranging from 11.70–41.24°. The intensity data were collected using the ω -2 θ scan technique with one standard reflection measured every 50 counts without significant variation. Corrections for Lorentz and polarization effects were applied, and absorption was corrected using the empirical Walker and Stuart method¹³ with T_{\min} = 0.883 and T_{\max} = 0.984. The structure was solved by the direct method, using the SHELXS86 program¹⁴ and refined subsequently by the full-matrix least-squares program SHELX96.¹⁵ Hydrogen atoms were introduced in calculated positions using a riding model with fixed C–H distances (0.93 Å for C_{sp2}, 0.97 Å for CH₂ and 0.96 Å for CH₃). Overall isotropic displacement parameters were refined for different CH types. The residual electron density on the final difference map was between 1.40 and –2.32 e Å⁻³, and the highest peaks were found at 0.97 and 0.91 Å from the platinum atom. One ethyl group including the C13 and C14 atoms showed considerably greater thermal displacement parameters than any other part of the molecule suggesting possible disorder, but a careful inspection of the difference map did not indicate any resolved alternate locations for these atoms. Introducing the suggested split sites for these atoms given by the program did not improve the refinement results. Molecular drawings were produced by the ORTEP¹⁶ and PLUTON programs.¹⁷ The final atomic parameters with equivalent isotropic thermal parameters are given in Table II. Additional X-ray crystallographic data, *i.e.* the full table of bond distances and bond angles, torsion angles, table of anisotropic thermal parameters, hydrogen atomic coordinates with isotropic thermal parameters and lists of structure factors (7 pages) have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained on request, free of charge, by quoting the publication citation and the deposition number 103231.

TABLE I
Crystal data and structure refinement details

Formula	Pt[Cl ₂ (C ₁₄ H ₁₈ NO ₃ P) ₂]
M_r	824.52
Crystal size / mm	0.3 × 0.4 × 0.8
Space group	$P\bar{1}$
$a / \text{Å}$	10.806(2)
$b / \text{Å}$	9.111(2)
$c / \text{Å}$	8.888(2)
$\alpha / ^\circ$	115.21(3)
$\beta / ^\circ$	93.68(4)
$\gamma / ^\circ$	96.28(2)
$V / \text{Å}^3$	781.0(3)
Z	1
$D_c / \text{Mg m}^{-3}$	1.753
Radiation	Cu-K α
$F(000)$	408
μ / mm^{-1}	11.313
T / K	293(2)
Index ranges	-13 < h < 12 -11 < k < 9 -10 < l < 8
Scan mode	ω -2 θ
T_{\min}, T_{\max}	0.883, 0.984
Reflections measured	2963
Reflections observed	2963 [$I > 2\sigma(I)$]
Refined parameters	191
R	0.0302
wR	0.0794
w	$1 / [\sigma^2(F_o^2) + (0.0689P)^2 + 1.01P]$
P	$(F_o^2 + 2F_c^2) / 3$
$\Delta\rho_{\max, \min} / \text{e Å}^{-3}$	1.399, -2.321
$(\Delta / \sigma)_{\max}$	0.001

RESULTS AND DISCUSSION

The molecular structure with the atom numbering scheme is depicted in Figure 1. Some interesting bond distances and bond angles are given in Table III.

The complex has a *trans* configuration. The coordination about platinum, which is situated in the crystallographic centre of symmetry, is essen-

TABLE II
Atomic coordinates ($x, y, z \times 10^4$) and equivalent isotropic displacement parameters ($U_{\text{eq}} \times 10^3 / \text{\AA}^2$)

Atom	x	y	z	U_{eq}
Pt1	0	0	0	26(1)
Cl1	1594(1)	911(1)	-1142(2)	39(1)
P1	2851(1)	2008(2)	4190(2)	42(1)
O1	3718(4)	1134(6)	2848(6)	66(1)
O2	3384(4)	1836(7)	5775(6)	72(1)
O3	2732(5)	3681(5)	4454(6)	66(1)
N1	941(3)	-1852(4)	-78(5)	32(1)
C1	995(5)	-2930(6)	-1651(6)	39(1)
C2	1352(5)	-4473(6)	-2113(7)	46(1)
C3	1601(5)	-4955(6)	-903(8)	46(1)
C4	1578(4)	-3878(6)	772(7)	40(1)
C5	1308(4)	-2254(5)	1211(6)	32(1)
C6	1425(4)	-1129(6)	2931(6)	38(1)
C7	1691(5)	-1711(8)	4109(7)	51(1)
C8	1889(5)	-3320(8)	3677(9)	58(2)
C9	1858(5)	-4374(7)	2055(9)	53(1)
C10	1380(5)	683(6)	3580(6)	42(1)
C11	4297(6)	1847(11)	1844(9)	70(2)
C12	5652(7)	2335(12)	2358(12)	85(2)
C13	4617(8)	2618(18)	6646(13)	129(5)
C14	4831(8)	2638(17)	8135(12)	120(4)

tially square planar. The 8-dqmp molecule is bonded to platinum as a monodentate ligand through its nitrogen atom. The Pt1–N1 bond distance of 2.042(4) Å is similar to the corresponding values reported in closely related complexes, *i.e.* with the formamidine ligand¹⁸ ranging from 2.014(8) to 2.045(8) Å, in *trans*-dichlorobis(thiazole)platinum(II) of 2.02(2) and 2.08(2) Å.¹⁸ The Pt–Cl separation of 2.306(1) Å is typical of a *trans* Cl–Pt–Cl arrangement.^{18–21}

The quinolyl moiety in the complex is not planar with respect to the coordination plane. The observed twisting angle of 65.1(1)° probably stems from steric factors and this rotation about the Pt1–N1 bond brings even two hydrogen atoms into a position for interactions with the metal atom: the Pt1–H10B distance is 2.309(5) Å, while the Pt1–H1 distance is 2.746(5) Å. This is consistent with some other observations from the literature for *trans*-PtCl₂X₂ complexes, where the reported values are 2.44,²⁰ 2.43²¹ and

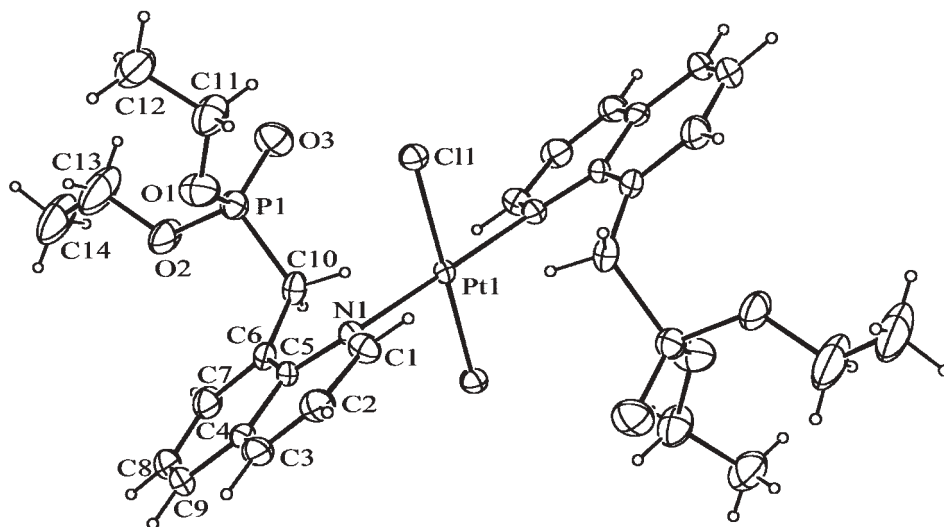


Figure 1. Molecular structure of the complex with displacement ellipsoids shown at the 30% probability level.

TABLE III
Selected geometric parameters

Bond lengths / Å			
Pt1–N1	2.042(4)	N1–C5	1.391(6)
Pt1–Cl1	2.305(1)	O1–C11	1.445(8)
P1–O3	1.461(4)	O2–C13	1.440(9)
P1–O1	1.560(4)	C6–C10	1.507(7)
P1–O2	1.564(4)	C11–C12	1.466(10)
P1–C10	1.786(5)	C13–C14	1.321(12)
N1–C1	1.332(6)		
Bond angles / deg			
N1–Pt1–Cl1	89.8(1)	C11–O1–P1	123.7(5)
N1–Pt1–Cl1#i	90.2(1)	C13–O2–P1	122.2(5)
O3–P1–O1	114.7(3)	C1–N1–Pt1	111.4(3)
O3–P1–O2	115.3(3)	C5–N1–Pt1	129.2(3)
O1–P1–O2	104.0(3)	C6–C10–P1	116.8(3)
O3–P1–C10	113.1(3)	O1–C11–C12	111.3(6)
O1–P1–C10	106.3(3)	O2–C13–C14	114.6(8)
O2–P1–C10	102.2(2)		

Symmetry transformations used to generate equivalent atoms: #i $-x, -y, -z$.

2.53 Å.²² Namely, the number of different ligands and complexes show detectable weak Pt ← H–C interactions. In all cases where crystallographic support is available, the C–H vector faces toward the metal and occupies a pseudoaxial position above the coordination plane, with Pt–H separations often in the range of 2.3–2.9 Å.²² The hydrogen atom of prime interest here, H10B, has a position entirely consistent with this kind of interaction. In the refinement of the structure with the position of H10B located in the difference map and refined without any constrain, the actual Pt1–H10B distance has the shortest value reported until now – 2.09(7) Å, while C10–H10B is elongated to 1.21(7) Å.

The cited H10B makes a weak intramolecular interaction with the Cl atom of 2.927(5) Å, which is close to the sum of the hydrogen and chlorine van der Waals radii (3.0 Å)²³ and can be considered a possible hydrogen bond.

The structure shows that the ligand has a short P=O distance for the phosphoryl group (P1–O3 = 1.461(4) Å) and longer distances between the P–O atoms of the phosphonate groups (P1–O1 = 1.560(5) and P1–O2 = 1.564(4) Å). The geometry around the P atom deviates from the regular tetrahedron according to the pattern typical of phosphate diesters, *i.e.* angles involving »long« ester P–O bonds are smaller [102.2(2)–106.3(3)°] and others involving the phosphoryl group are larger [113.1(3)–115.3(3)°] than the ideal value of 109.5°. The unusual C–C bond distances and/or the great thermal motions were observed in many similar diethyl phosphonate moieties.^{24–30} We also noticed the same behavior in our previous structures with the same ligand in Pd(II) complexes¹¹ and for diethyl 2-quinolylmethylphosphonate ligand in the PdCl₂ and PdBr₂ complexes.¹⁰

Acknowledgements. – The financial support granted by the Ministry of Science, Technology and Informatics of the Republic of Croatia is gratefully acknowledged.

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SAŽETAK

**Sinteza te kristalna i molekulska struktura *trans*-[PtCl₂(8-dqmp)₂]
(8-dqmp = diethyl 8-quinolylmethylphosphonate)**

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Pripravljen je kompleks *trans*-[PtCl₂(8-dqmp)₂], a rentgenskom strukturnom analizom određena je molekulska i kristalna struktura. Atom platine ima malo iskrivljenu planarnu *trans*-konfiguraciju s Pt1–N1 = 2,042(4) i Pt1–Cl1 = 2,306(1) Å. Diedarski kut između ravnine položene atomima Pt1, Cl1 i N1, te najbolje ravnine 8-metilkinolinskog prstena iznosi 65.1(1)°. Kompleks ima vrlo zanimljivu značajku, tj. razmjerno kratku interakciju metilenskog vodika H10B s atomom platine od 2.309(5) Å, stvarajući tako dodatne, približno aksijalne položaje oko centralnog metalnog atoma. Utočnjavanje metodom najmanjih kvadrata dalo je konačnu vrijednost faktora *R* od 3,02%.